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TIME SCALE OF THE THREE-PHASE CONTACT FORMATION BY THE BUBBLE COLLIDING WITH HYDROPHOBIC SURFACE IN N-PENTANOL AND N-OCTANOL SOLUTIONS

Phenomena occurring during collisions of the bubble rising in distilled water, n-pentanol and n-octanol solutions with hydrophobic Teflon plates of different roughness were studied using high-speed Camera (1182 Hz). It was found that even in the case of such hydrophobic solid surface as Teflon the bubble attachment didn't need to occur at first collision. In distilled water the bubble could bounce a few times without attachment. Presence of surface active substance facilitated the attachment as well as lowered the bubble local velocity. Time-scale was shortened in the case "medium rough" Teflon from ca. 40 ms (in distilled water) to 16 ms (in the case of 0.00003 M n-octanol solution), while at the "rough" surface the attachment occurred in 4 ms in both systems. It was observed that surface roughness and presence of gas bubbles at Teflon surface were crucial for the time-scale of the bubble attachment. With increasing surface roughness and immersion time into solution of the Teflon plate the probability that the bubble be attached at once was increased.

INTRODUCTION

In flotation air bubbles are introduced into the pulp to collect grains of useful component and transport them to froth layer. Flotation separation is due to differentiation in surface properties of grains of gangue (waste) and useful components of the ore. Collecting reagents are added to selectively adsorb and make the surface of useful component grains hydrophobic enough for their attachment to the gas bubble, while frothers should assure formation of froth layer and facilitate the

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grains attachment (Leja, 1982). As written by Vera et. al., (1998) from a perspective of hydrophobic particle the flotation process can be divided into a sequence of four following sub-processes: i) collision of bubble and particle, attachment of particle to bubble, iii) transport of particle-bubble aggregate to the pulp-froth interface, and iv) recovery of particle to concentrate launder. Bubbles rising inside flotation cell must collide with the solid particle first and then the attachment of the bubble to solid surface must take place (Leja, 1982; Ralston and Dukhin, 1999; Nguyn and Schulze, 2004). If detachment (Stechemesser and Nguyen, 1999; Phan *et al*., 2003; Nguyn and Schulze, 2004), i.e. the third (after collision and attachment) governing effect of this elementary step of flotation (Leja, 1982) does not occur then the stable bubble-grain aggregate formed floats to the froth layer. For efficient capture of grains by the rising bubble they must first undergo a sufficiently close – this process is governed by the fluid mechanics of the particle in the long-range hydrodynamic force field around the bubble (Stechemesser and Nguyen, 1999; Phan *et al*., 2003; Nguyn and Schulze, 2004). When the distance between the bubble and mineral particle becomes shorter then the atomic, molecular and surface forces become are significant and the attachment process starts.

Successful attachment consists of three steps (Stechemesser and Nguyen, 1999; Ralston and Dukhin, 1999; Yoon, 2000; Phan *et al*., 2003; Ralston *et al.*, 2003; Nguyn and Schulze, 2004): i) thinning of the thin liquid intervening film between the bubble and the grain to the critical thickness (h_{cr}), ii) rupture of the liquid film and formation of the three-phase contact nucleus, iii) expansion of the three-phase contact to form a stable aggregate. If the solid surface is hydrophilic then the formation of the bubble-particle aggregate should not happen, because the thin liquid layer between the bubble and the grain is stable. For hydrophobic particles we have the opposite situation – the intervening liquid film is of much lower stability. That is why after the bubble collision with hydrophobic grain the intervening film drains until a critical thickness is reached and then the film ruptures. The detachment process is governed by hydrodynamics conditions of the system, capillary forces and the particle size.

The paper presents results of studies on attachment dynamics of the bubble colliding with hydrophobic solid plates in n-pentanol and n-octanol solutions. Teflon was used as a solid having model hydrophobic surface and three plates of different roughness were used to investigate effect of the surface roughness. Influence of time of the plate's immersion into solution on time scale of the bubble attachment was studied, as well.

EXPERIMENTAL

The experimental set-up used is presented schematically in Fig.1. Its main components are: i) a square glass column with capillary of inner diameter of 0.075 mm at the bottom, ii) syringe pump for gas supply, iii) high-speed camera for recording the bubble collisions with the solid plates, iv) PC with image analysis

software. High-speed (1182 frames per second) SpeedCam 512+ camera was used to monitor and record processes occurring during the bubble collision with the Teflon plates mounted at the distance ca. 300 mm from the capillary. The movies recorded were transformed into BMP pictures and analyzed using the SigmaScanPro Image Analysis Software (Krasowska *et al.*, 2004; Malysa *et al*., 2005). The bubble velocity variations during collisions with the liquid/solid interface were determined by measurements coordinates of the bubble bottom pole on every subsequent frame of the camera recording.
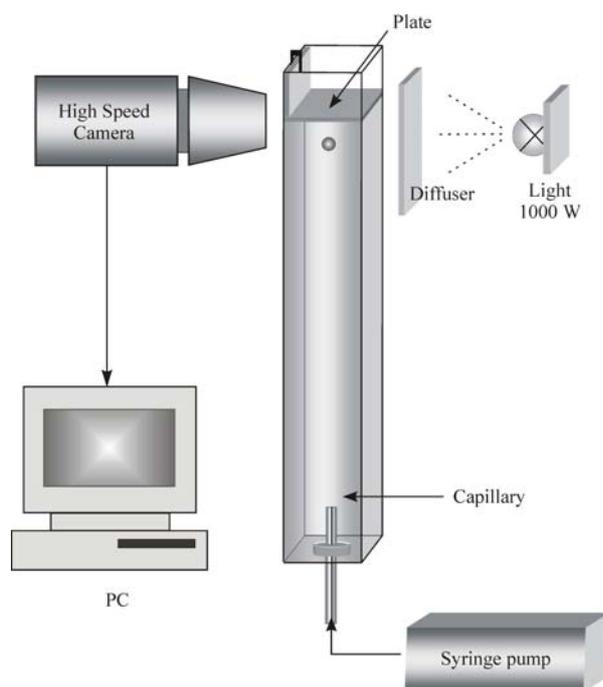

Fig. 1.Schematic of the experimental set-up

Microscopic photos of surfaces of the three different roughness Teflon plates used in the experiments are showed in Fig. 2. First plate (Fig. 2a), called "polished" Teflon, had the surface polished using the abrasive no. 2400 and diamond grinding DP-Paste ¼ μm. The second one (Fig. 2b), called "medium rough" was a commercial Teflon surface neither polished nor roughened. The third plate (Fig. 2c), called "rough" Teflon was treated with abrasive paper no. 100.

Four-times distilled water and high purity n-pentanol and n-octanol were used for solution preparation. The Teflon plates were cleaned with a chromic mixture and carefully washed-out with four-time distilled water. The experiments were carried out in room temperature.
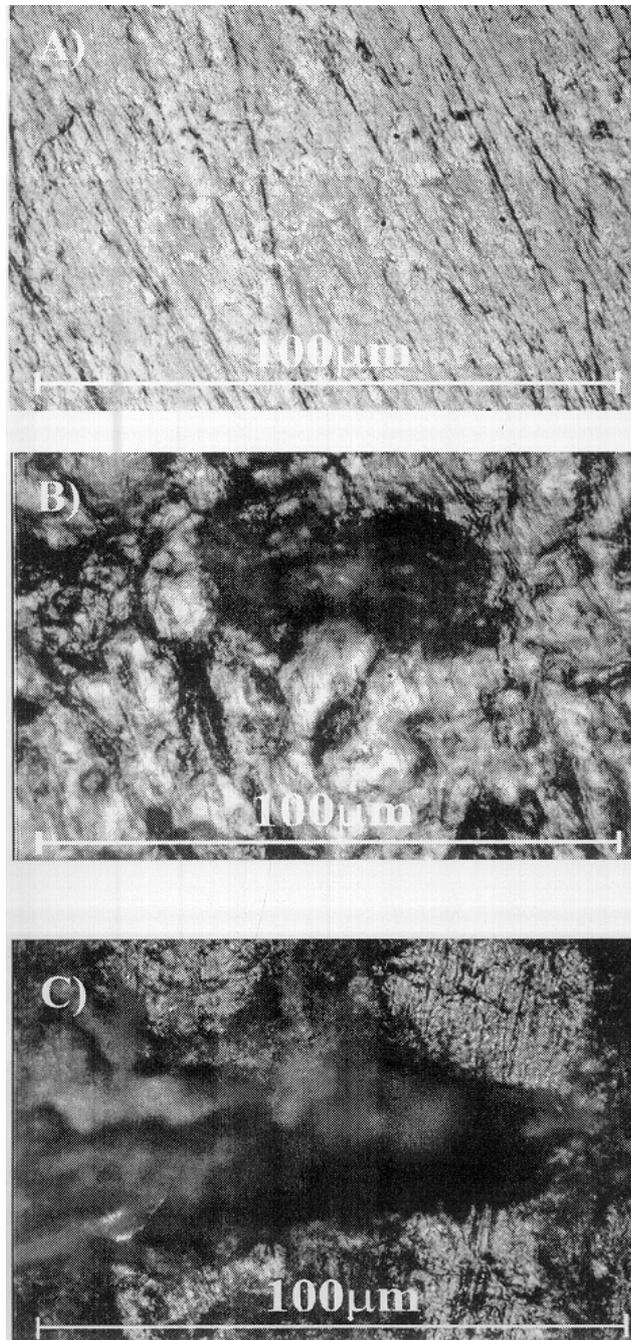
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Fig. 2. Microscopic photos of surfaces of the "polished" (A), "medium rough" (B) and "rough" (C) Teflon plates

RESULT AND DISCUSSION

In real flotation systems the grains are much smaller than bubbles and probability of formation of the stable bubble-grain aggregates is a product of probabilities of collision, attachment and that detachment does not occur (Derjaguin and Dukhin, 1960; Schimmoler et. al., 1993; Ralston and Dukhin, 1999). In our model system the bubble must always collide with the solid plate because its dimensions were much larger than diameter of the rising bubble diameter. It means that the collision probability was always 100% and similarly probability that detachment does not occur was also 100% (buoyancy force squeezes the bubble attached to plate). Thus, data obtained in our model system enable revealing factors governing formation of the phase contact during bubble collision with hydrophobic solid surface.
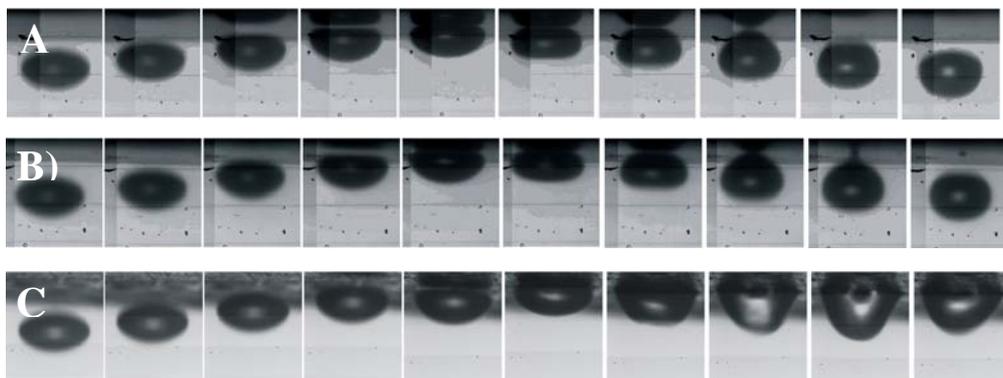

Fig. 3. Sequences of the photos (time interval = 0.845 ms) illustrating bouncing of the bubble from the "polished" Teflon surface (A), "medium rough" (B) and the three-phase contact formation at the "rough" Teflon surface (C) during the first collision in distilled water

Figure 3 presents sequences of photos, showing phenomena occurring when the rising bubble collided with "polished" (Fig. 3a), "medium rough" (Fig. 3b) and "rough" (Fig. 3c) Teflon surfaces in distilled water. It is rather commonly assumed that when the solid surface is hydrophobic enough then during collision with bubble the attachment should occur at once, while in the case of hydrophilic solid surface the attachment should not occur at all. However, as can be seen in Fig. 3, neither in the case of the "polished" (Fig. 3a), nor "medium rough" (Fig. 3b) Teflon surface sthe attachment occurred during the first bubble approach to the liquid/solid interface. After collision the bubble bounced backward and its shape pulsated rapidly within time intervals shorter than 0.845ms.

To form the three phase contact a liquid film separating the colliding bubble from solid surface must reach a critical thickness of its rupture (Mahnke *et al.*, 1999; Exerowa *et al.*, 2003). According to the DLVO theory there are two main components determining stability of thin liquid films: i) the electric double layer repulsions arising

from the surface charges at interfaces (range of this repulsion interaction is of an order 1-100 nm), and ii) van der Waals attractions (with a range of interaction about 1 nm). During last ca. 30 years there was a lot of studies showing existence of long range attraction (10-100 nm) between the hydrophobic solid surfaces immersed into solutions - so-called "long-range hydrophobic forces". Recently, however, it was showed (Parker *et al.*, 1994; Ishida *et al.*, 2000; Schulze *et al.*, 2001; Attard, 2003) that the concept of the hydrophobic forces existence was not correct. Parker *et al.*, (1994), Ishida *et al.*, (2000) and Attard (2003) showed, using the taping mode AFM, that submicroscopic gas bubbles (of size depended on hydrophobicity and smoothness of the solid surface) were always present at the hydrophobic surface immersed in solution. It was pointed out that the origin of this so-called "long-range hydrophobic forces" was in reality due to bridging of the nanobubbles present at the hydrophobic surfaces immersed into aqueous solutions. Results of our studies on dynamics of the bubble attachment to hydrophobic Teflon surface (Krasowska *et al.*, 2004; Malysa *et al.*, 2005) indicate also on importance of submicroscopic bubbles presence in formation of the three phase contact. As can be noted in Fig. 3b ("medium rough" Teflon surface) a "satellite micro bubble" was left at the Teflon surface by the bouncing bubble. When during the second approach the bubble hit exactly the same point, i.e. at the satellite microbubble left, then the attachment occurred, while in the case of the "polished" Teflon surface it did not happen during the second, third or even fourth collision (see Fig. 4). In the case of "rough" Teflon surface (Fig. 3c) the attachment occurred during the first collision. Magnification of our camera optics is not large enough to enable detection of microbubbles present at the hydrophobic Teflon surface, but a careful examination of the photos obtained indicates on presence of some small bubbles at the "rough" Teflon surface prior to the bubble collision (compare Fig. 3c and 3b). These data indicate that indeed, microbubbles present at the Teflon surface facilitate the three-phase contact formation.

Results of quantitative analysis of the velocity variations during the bubble collisions with the "polished" (circles), "medium rough" (diamonds) and the "rough" (triangles) Teflon surfaces in distilled water are presented in Fig. 4. In distilled water the bubble equivalent diameter was 1.48±0.03 mm and its terminal velocity was 34.8±0.3 cm/s. During the first collision with the solid plates the bubble was rapidly stopped and within time period of ca. 4 ms its velocity was changed from. +35 to ca. -30 cm/s (see Fig. 4). In the case of "rough" Teflon the three-phase contact was formed during the first collision (see TPC (3) in Fig. 4) and the bubble stayed attached. Bouncing backwards and clear separation from the plate took place for both "polished" and "medium rough" Teflon. Then, the bubble started its second approach towards these Teflon plates reaching the approach velocity of 24 cm/s (see Fig. 4). During the second collision the bubble attachment to the "medium rough" Teflon plate occurred (TPC (2) in Fig. 4), while in the case of "polished" Teflon a few more "approach-bouncing" cycles could be noted. Velocity of the bubble colliding with the "polished" Teflon decreased with every "approach-bounce" cycle as a result of the

energy dissipation. During the fifth collision the thin liquid film between bubble and "polished" Teflon surface ruptured and the three-phase contact formation was observed (TPC (1) in Fig. 4).
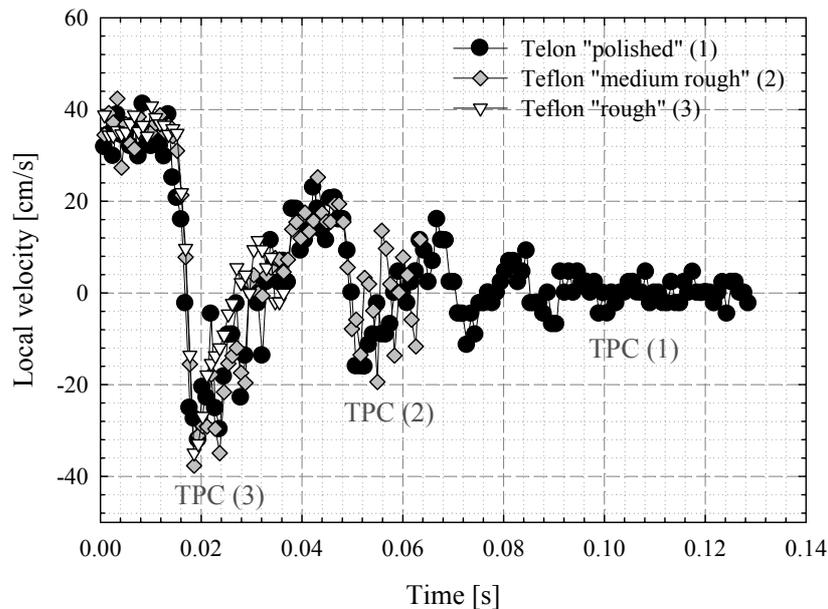

Fig. 4. Variations of the bubble local velocity during collisions with the "polished" (circles), "medium rough" (diamonds) and "rough" Teflon (triangles) surfaces in distilled water

Let's evaluate the time-scale of the bubble attachment (three-phase contact formation) for these three exemplary cases. The shortest time of ca. 4ms was needed in the case of "rough" Teflon surface. In the case of the "medium rough" Teflon the time needed was ca. 40ms. This was the time period from the first contact of the bubble with the plate till its attachment. The longest time (80 ms) was necessary for the three-phase contact formation during the bubble collision with the "polished" Teflon plate. It needs to be added here that reproducibility of the attachment experiments was rather low, especially in the case of the "medium rough" Teflon surface. We think that this is due to dynamics (rapidity) of these processes and/or local inhomogeneities of the solid surfaces, and/or presence of various sizes of gas nuclei (nanobubbles), etc. In the case of "rough" Teflon, the results were very well reproducible and the three-phase contact always occurred during the first collision of the rising bubble. In the case of the "polished" Teflon the probability that the three-phase contact is formed during first, second or even third collision was zero, i.e. the attachment occurred only at fourth collision or even later. Lowest reproducibility was observed in the case of the "medium rough" Teflon and the statistics of the

attachments is presented in Table 1. Most probable this lowest reproducibility is due to local differences in roughness and/or size and number of submicroscopic bubbles present at the surface.

Table 1. Statistics of the bubble attachment during collisions in distilled water with the "medium rough" Teflon

V_{term} [cm/s]	Attachment during [%]				
	$1^{s}t$	2nd	3rd	4th	No. of experiments
34.8	5	55	15	25	40

Presence of n-pentanol and n-octanol lowers significantly the bubble velocity, i.e. kinetic energy of the bubble colliding with liquid/solid interface is lowered. Figure 5 presents the velocity variations during the bubble collisions with the Teflon plates in 0.00003M n-octanol solutions. As seen the bubble approach velocity was 14.9 cm/s ± 1.3 cm/s, i.e. over two times lower than in distilled water. The attachment to the "rough" Teflon surface occurred during the first collisions (triangles in Fig. 5).
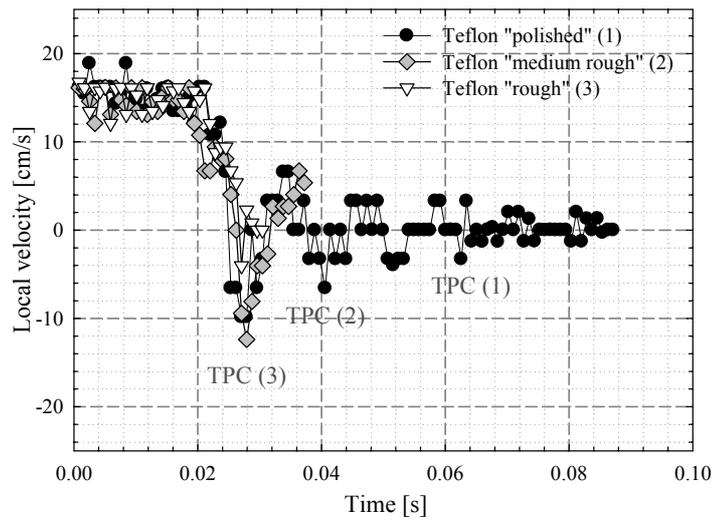

Fig. 5. Variations of the bubble local velocity during collisions with the "polished" (circles), "medium rough" (diamonds) and "rough" Teflon (triangles) surfaces in 0.00003 M n-octanol solution

In the case of the "medium rough" surface (diamonds in Fig. 5) the three-phase contact and the bubble attachment took place during the second collision, while there were observed three "approach-bounce" cycles prior to attachment to the "polished" Teflon surface, which occurred during the fourth bubble approach. Thus, qualitatively the picture is similar as in distilled water. However, in n-octanol solutions the time-

scale of the three-phase contact formation, i.e. time period from the moment of the bubble first collision till the attachment, was significantly shortened in the case of the "polished" and "medium rough" Teflon surfaces. In the case of the "rough" Teflon surface the bubble attachment occurred during the first collision and its time-scale was similar as in distilled water, i.e. ca. 4 ms. For the "medium rough" Teflon the time-scale of the attachment (TPC (2) in Fig. 5) was 16 ms, i.e., about two times shorter than in water (compare with TPC (2) in Fig.4). The longest time (ca. 40 ms) was needed for the bubble attachment to the "polished" Teflon surface, but again about two times shorter than in distilled water. This shortening of the time needed for attachment is most probable caused by lowering of the bubble approach velocity and amplitude of the "approach-bounce" cycles. Lower velocity (kinetic energy) means that the time of the bubble-solid contact is prolonged, i.e. time available for syneresis of the intervening liquid film is prolonged and the thinning liquid film can reach its critical thickness of rupture.
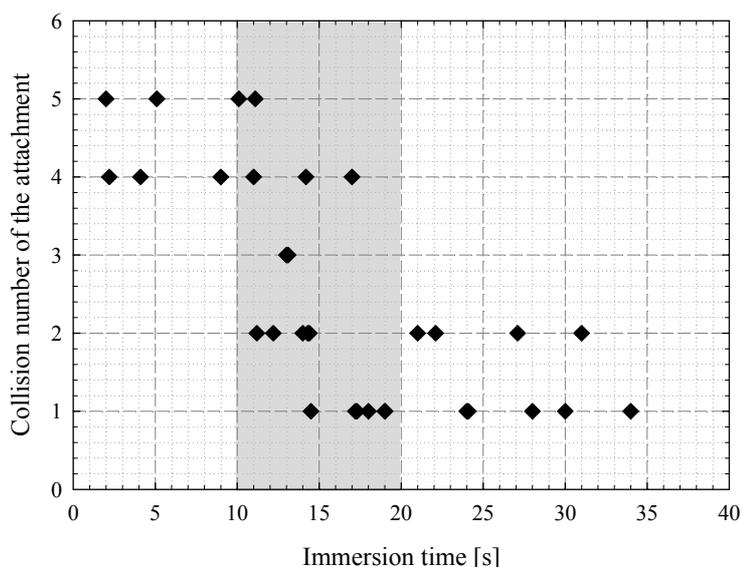

Fig. 6. Influence of immersion time on collision number of the approach during which the bubble was attached to the "medium rough" Teflon plate in 0.0001 M n-pentanol solution

As discussed above, presence of submicroscopic bubbles at hydrophobic Teflon surfaces facilitates, in our opinion, the bubble attachment and can be also one of the reasons of scatter of the experimental results. To check this hypothesis a few series of experiments was carried out, where time-scale of the attachment was determined as a function of immersion time of the "medium rough" Teflon plate into n-pentanol and n-octanol solutions. At longer immersion time the probability of gas nucleation and

nanobubbles coalescence (lateral bridging) (Yang *et al.*, 2003) at Teflon surface should be higher and it should facilitate the bubble attachments. Data presented in Fig. 6 confirm correctness of this hypothesis. There are presented collision number (during which the bubble was attached) as a function of the immersion time for the "medium rough" Teflon plate in 0.0001M n-pentanol solution. There can be clearly noted, despite data scatter, that the experimental results can be divided into two classes: i) one, for the immersion time $t_{im.} \leq 10$ s, and ii) the other, for $t_{im.} \geq 20$ s. After longer immersion time ($t_{im.} \geq 20$ s) the attachment occurred during the first or second collision, while when $t_{im.} \leq 10$ s then the probability that the three-phase contact would be formed during the first or second collision was zero – the bubble attachment occurred after more than three collisions. Data for n-octanol solutions of various concentrations are collected in Table 2. It can be noted there that with immersion time prolongation the probability of the bubble attachment during the first and second collisions was significantly increased. Thus, one can say that this is a general tendency being a strong indication that indeed, the bubble attachment is facilitated by a presence of submicroscopic bubbles at Teflon surface.

Table 2. Statistics of the bubble attachment during collisions in n-octanol solutions with the "medium rough" Teflon

Concentration [mol/dm³]	$\theta_{ads.}$ [%]	V_{term} [cm/s]	Attachment during [%]									
			1st		2nd		3rd		4th		No. of experiments	
			$t_{im} \leq 10s$	$t_{im} \geq 20s$	$t_{im} \leq 10s$	$t_{im} \geq 20s$	$t_{im} \leq 10s$	$t_{im} \geq 20s$	$t_{im} \leq 10s$	$t_{im} \geq 20s$	$t_{im} \leq 10s$	$t_{im} \geq 20s$
$3 \cdot 10^{-6}$	0.22	33.2	-	14.3	5.3	33.3	73.7	23.8	21	28.6	19	21
$6 \cdot 10^{-6}$	0.45	25.8	-	20	9.5	45	23.8	15	66.7	20	21	20
$3 \cdot 10^{-5}$	2.28	14.9	-	22.7	5.6	45.5	27.8	18.2	66.6	13.6	18	22
$9 \cdot 10^{-5}$	7.26	14.8	-	27.8	4.3	-	17.4	33.3	78.3	38.9	23	18
$3 \cdot 10^{-4}$	30.46	14.8	-	14.3	76.2	76.2	23.8	9.5	-	-	21	21
$6 \cdot 10^{-4}$	70.94	14.8	-	4.8	89.5	95.2	10.5	-	-	-	19	21

CONCLUDING REMARKS

Bubble colliding with even such model hydrophobic surface as the Teflon surface can bounce backwards a few times prior to the three-phase contact formation and attachment. Time-scale of the bubble attachment depended strongly on: i) surface roughness, ii) time of the plate immersion into aqueous solutions, and iii) concentration of n-pentanol and n-octanol solutions. Number of "approach-bouncing" cycles was decreasing with increasing roughness of the Teflon surface. It was found that prolongation of the immersion time of the Teflon plate into solution shortened time-scale of the bubble attachment. Presence of n-pentanol and n-octanol caused

about twofold shortening time-scale of the attachment due to, mainly, lowering the bubble approach velocity.

The data obtained indicate that a presence of the submicroscopic bubbles at the Teflon surface is of crucial importance for the three-phase contact formation and the bubble attachment. At higher surface roughness there is higher probability that microbubbles will stay attached to hydrophobic Teflon surface being immersed into solution. Similarly a longer immersion time is advantageous for gas nucleation and nano-bubble coalescence.

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Krasowska M., Malysa K., *Czas tworzenia kontaktu trójfazowego podczas kolizji bańki z powierzchnią hydrofobową w roztworach n-pentanolu i n-oktanolu,* Physicochemical Problems of Mineral Processing, 39 (2005) 21-32 (w jęz. ang)

Przy użyciu szybkiej kamery (1182 klatki na sekundę) badano procesy zachodzące podczas kolizji bańki z hydrofobowymi płytkami teflonowymi o różnym stopniu szorstkości. Pomiary wykonano w wodzie destylowanej oraz w roztworach n-pentanolu i n-oktanolu. Zaobserwowano, że nawet przy tak

hydrofobowej powierzchni, jaką jest Teflon, przyczepienie bańki nie musi nastąpić podczas pierwszej kolizji. W wodzie destylowanej bańka może odbić się kilkakrotnie zanim utworzy się kontakt trójfazowy. Obecność substancji powierzchniowo aktywnej przyspiesza przyczepienie bańki, jak również zmniejsza jej prędkość. Ze wzrostem szorstkości badanych powierzchni ulegał skróceniu czasu potrzebny do utworzenia kontaktu trójfazowego i przyczepienia bańki do powierzchni teflonu. W przypadku teflonu „o średnim stopniu" szorstkości powierzchni czas ten został skrócony z 40 ms (dla wody destylowanej) do 16 ms (dla 0.00003 M roztworu n-oktanolu). W przypadku teflonu "szorstkiego" zarówno dla wody destylowanej, jaki i 0.00003 M roztworu n-oktanolu czas potrzebny do utworzenia kontaktu trójfazowego wynosił 4ms. Szorstkość powierzchni i obecność mikro-pęcherzyków na badanych powierzchniach teflonu wydają się być kluczowymi czynnikami decydującymi o czasie tworzenia kontaktu trójfazowego. Wraz ze wzrostem szorstkości powierzchni oraz wydłużaniem czasu immersji płytki w roztworze ulegał skróceniu czas potrzebny do przyczepienia bańki.